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INTERFACIAL THERMODYNAMICS AND ADSORPTION
1. An Introduction to Surface Energetics and A Survey of Temperature Dependence Studies

C.W. Angle

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INTERFACIAL THERMODYNAMICS AND ADSORPTION
1. An Introduction to Surface Energetics and a Survey of Temperature Dependence Studies

by

Chandra Angle*

ABSTRACT

Colloids are part of many disciplines of applied science and everyday technology products. Interfacial properties dominate the behaviour of colloidal systems. To understand these systems, a thorough appreciation of interfacial thermodynamics is useful, especially when adsorption occurs.

The principles that govern interfaces of liquid/liquid, liquid/solid and liquid/vapour systems are discussed in relation to adsorption and the Gibbs Surface Excess. The Guggenheim-Adams model is compared with the Gibbs model. The former becomes more complex in mathematical treatment for liquid/liquid systems, especially if polymers are considered as the adsorbate. When the interphase volume is significant, the former is useful. Where simplicity and generality are required, the latter model is suitable. Special features of adsorption relative to thermodynamic properties, problems and assumptions for complex heterogeneous systems are discussed. Heats of immersion and heat capacities are shown to be useful in determining surface tension of solids of the same material.

The influence of temperature increase on surface entropy of liquid/vapour and liquid/liquid interfaces is surveyed with examples taken from many disciplines. Classical empirical relations developed in the past are illustrated in examples taken from metallurgy and heat transfer studies. Surface entropy as influenced by changes in adsorption with increased temperature is discussed in relation to polarography, polymers, proteins, surfactants and emulsions. Special emphasis is given to enhanced oil recovery.

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*Fuel Scientist, Coal Research Laboratories, Fuel Processing Laboratory, CANMET, Energy, Mines and Resources Canada.

PROPRIÉTÉS THERMODYNAMIQUES DE L'INTERFACE DES SYSTÈMES ET ADSORPTION

1. Introduction au comportement énergétique de l'interface et survol des études de la fonction de la température

par

Chandra Angle*

RÉSUMÉ

L'étude des colloïdes fait partie intégrante de plusieurs disciplines des sciences appliquées. Les colloïdes sont également des composantes de produits techniques d'usage courant. Les propriétés de l'interface contrôlent le comportement des sytèmes colloïdaux. Pour comprendre ces systèmes, il est nécessaire de connaître à fond les propriétés thermodynamiques de l'interface, particulièrement au moment de l'adsorption.

Les principes qui régissent les interfaces des systèmes liquide/liquide, liquide/solide et liquide/vapeur sont étudiés en fonction de l'adsorption et du modèle "Surface Excess" de Gibbs. On établit une comparaison entre le modèle Guggenheim-Adams et le modèle Gibbs. Le modèle Guggenheim-Adams s'avère plus complexe dans le cas du traitement mathématique des systèmes liquide/liquide, en particulier quand on tient compte du fait que la substance adsorbée consiste de polymères. Ce modèle est utile quand le volume de l'interphase est important. Cependant quand il s'agit d'opérations plus simples ou à caractère plus général, le modèle Gibbs convient davantage. Un survol des caractéristiques d'adsorption particulières en fonction des propriétés thermodynamiques, des problèmes, et des hypothèses sur les systèmes hétérogènes complexes est présenté. La chaleur de l'immersion et les capacités thermiques sont utiles pour déterminer la tension superficielle des solides qui ont une même composition.

Une étude de l'effet de l'augmentation de la température sur l'entropie de la surface des interfaces liquide/vapeur et liquide/liquide est présentée et illustrée par des exemples tirés de nombreuses disciplines. Les relations empiriques classiques établies antérieurement sont illustrées par des exemples ressortant d'études dans le domaine de la métallurgie et du transfert thermique. L'entropie de la surface influencée par les changements qui se produisent sur le plan de l'adsorption à des températures plus élevées est étudiée en fonction de la polarographie, des polymères, des substances protéiques, des surfactants et des émulsions. Une attention particulière est accordée à l'amélioration de la récupération de l'huile.

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*Scientifique de la recherche sur les combustibles, Laboratoire de traitement des combustibles, CANMET, Énergie, Mines et Ressources Canada.

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INTRODUCTION

Interfaces are boundaries between two phases within a system. These are classified as solid/liquid, liquid/liquid, liquid/vapor and solid/gas interfaces. In colloidal suspensions the interfacial properties are predominant over the bulk properties because of their large specific surface area, and thus surface properties dominate their behaviour. The 'solute' particle sizes are sufficiently small that they are not affected significantly by gravitational forces, and sufficiently large that there are marked deviations from the properties of typical solutions. The approximate size of colloidal particles are 10^{-9}m to 1µm (10^{-6}meter)

Because of the large size of colloids relative to molecules and ions in ordinary solutions, colloidal 'solutions' display: 1)very low osmotic pressure, 2) very low solute diffusion coefficients, 3) very low freezing point depressions, 4) they do not pass through dialysis membranes and are turbid, and 5) scatter light.

Knowledge of and understanding of interfaces are essential in many technologies such as food, paints, pesticides, agriculture, catalysis, emulsions, polymers, foams, detergents, and soaps. In pure science it has applications in nucleation, crystal growth, and biochemical systems.

Because of the technological importance of these systems a vast array of research and literature has centered around these interfaces. The interaction of material at the interface in adsorption forms surface films, and changes surface pressures. The associated interfacial energies relative to material in the bulk command attention. Matter at the interface displays different physical properties and energy characteristics from that of the bulk.

The surface chemistry of materials that are involved in interfacial phenomena is important in these relevant applications. Central to the understanding of the interface's surface chemistry is the surface thermodynamics. It provides insight into the energetics of surfaces as they are modified.

Particles with charged surfaces have electrical properties. They move in an electrical field. Knowledge of the surfaces of these particles is necessary for the full understanding of their behavior. However, particles without charges behave differently from charged particles. Particles in a

continuous medium display bulk properties as well as surface properties. Although charged particles in polar or charged electrolytes are very relevant to stability studies, their interfacial properties are more complex than uncharged systems.

SCOPE

In order to narrow the scope of this paper, surface electrochemistry and electrochemical thermodynamics are not addressed. This paper deals with the surface thermodynamics or energetics of the interface as it is modified by adsorption. The theories developed around the interfacial thermodynamics and adsorption are explored and compared. The responses of different systems with temperature variation are used as examples in demonstrating the usefulness of temperature dependance studies.

Interfaces classified as liquid/vapour (L/V), liquid/liquid (L/L), solid/vapour (S/V), and solid/liquid (S/L), appear in order of complexity both in behaviour and makeup. The boundary region where two phases meet has been described both mathematically (Gibbs dividing plane) and physically as an interface. "Surface" is used when one of the phases is a gas or vapour. When the region of the interface has thickness, it is called an "interphase" and is usually characterized by a gradation of property between the two bulk phases. In thermodynamic arguments "interface" is used, especially if a clear consideration of the boundary region thickness is required. Figure 1 shows a schematic of an interface both at S/L and L/L boundaries (2,14). The structure and energy of these interfaces are described sequentially, relating first L/V, then L/L and S/L.

Since adsorption is quite a complex field in itself, this paper will not address all aspects of adsorption. It seeks to establish some common principles which govern interfaces. Thus it presents background for the appreciation of published work in the field of surface science and adsorption.

Understanding the phenomenon of adsorption on a surface or interface requires knowledge of the surface and or interface both in structure and in energy. The changes in the energy of the system involved is manifested in the structural differences that occur before and after adsorption (Figs 1, 2a, 2b). The basic similarities between the various types of interfaces which were ignored in the past because of the limitations

inherent in the experimental procedures used in these studies have been treated by Kipling qualitatively (1). More recently Dabrowski et al (2) reviewed thoroughly and critically adsorption from nonelectrolyte liquid mixtures onto solid surfaces.They pointed out the common features of all the interfaces and the inherent complexities. This paper further simplifies and expands on the common features by which the interfaces at the solid and liquids may be approached, particularly adsorption and the Gibbs surface excess.

The influence of temperature changes on surface energetics and adsorption is surveyed in the last part of this paper and where appropriate earlier in the text. The literature published on the temperature effects is sparse yet diverse. It ranges from theoretical to applied surface studies. Examples quoted in the text are from the many walks of surface science. It is intended to provide simple but clear appreciation of surface thermodynamics in relation to adsorption in many disciplines. Of most relevance to the field of energy, is emulsification, surfactant adsorption, critical surface energies, and solid/liquid adsorption. The discussion of many aspects of work published in other disciplines provides insight into techniques and interpretation of data, that are useful in systems of immediate interest to applied surface science.

FUNDAMENTALS

SURFACE TENSION AND SURFACE ENERGIES-DEFINITIONS

In a pure liquid/vapor interface, the intermolecular van der Waal forces are normally unbalanced at the surface. The surface molecules experience a net pull into the bulk of the liquid. Energy is needed to transfer a molecule from the bulk of the solution to the interface. To increase the surface area of an interface, energy is required. The surface tension is considered as a "contractile skin" which has a property of contracting with the same forces per unit length. Surface tension denoted γ is treated as surface free energy per unit area in such pure systems. For example, to minimise surface energy a spherical shape with a minimum surface to volume ratio is assumed by a droplet in equilibrium with its vapour phase.

For a plane surface, surface tension is considered as a force acting parallel to the surface and at right angles to a line of unit length anywhere on the surface. The pressure of L/L or L/V phases which are separated by a plane dividing surface, are the same at equilibrium.

If the interface is not planar, a significant change in area results when the interface is displaced. The inequality of pressures on both sides of the interface results in curvature. Interfacial tension in this case is defined in terms of the radii of curvature and the different pressures (3,9,31). Curved interfaces are treated mechanically by Laplace and Kelvin equations (9). Except for very small radii, the magnitude of the surface tension is not a function of the curvature (3,8). For the purposes of this paper only plane surfaces will be considered.

Surface molecules are considered to be in a state of higher free energy (4) than their counterparts in the bulk liquid because they undergo fewer intermolecular interactions, than the bulk molecules.

This surface free energy is sometimes called excess free energy or Gibbs excess. This is the free energy change that occurs when there is isothermal reversible formation of a liquid surface as work must be done to increase the surface area (3). Surface excess free energy is an extensive property,and is dependent on the interfacial area of the system. The surface excess free energy is also called excess interfacial free energy when it is the free energy required to form a fresh interface. It is also considered the excess free energy which the molecules possess by virtue of their being in the surface/interface. It is not total free energy of the surface molecules, as will be shown later.

The specific free energy is an intensive thermodynamic property. When pure liquids are in equilibrium with their vapour, the units of surface tension and specific excess free energy are the same dimensionally and numerically. For two pure immiscible liquids which makes contact at a plane interface, the excess interfacial free energy equals the interfacial tension. This is not so for impure systems as will be shown later. In colloidal systems,there are processes which are classified by the changes of surface excess free energy resulting from the variation of the surface area, or the surface tension, or both.

The specific excess surface free energy of a pure solid is the work required to form a unit area of surface. This is equivalent to the surface

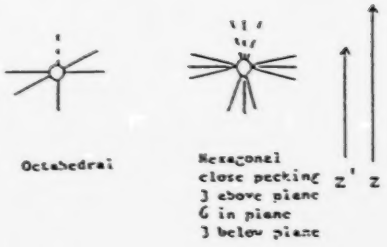
tension of an equilibrium isotropic surface. In the case of solids, in practice, the atoms and molecules in a solid surface freshly generated by cleavage are not in equilibrium positions because their mobility is very low. Surface tension in solids could be expressed as the the restoring force necessary to bring the freshly exposed surface to its equilibrium state. Here surface tension is a two dimensional negative pressure whose units (mNm^{-1}) then becomes analogous to bulk pressure units $(mNm^{-})^{2}$.

The surface of a liquid may be considered to be homogeneous with its properties remaining fairly constant across the surface. Because of fluidity, the homogeneous liquid surface is also considered to be energetically uniform on a submicroscopic level (not at molecular level). This is manifested in the heats of adsorption being fairly independent of the fraction of the surface covered (3). In contrast, solid surfaces are heterogeneous and are energetically non-uniform. The chemical nature and the adsorption characteristics vary from place to place across the surface. Heats of adsorption usually vary with the area of surface covered(4).
Since the rate at which atoms or molecules change position is a function of their molecular motions their dynamics play a role in the adsorption behaviour.

THE STRUCTURE AND ENERGETICS OF LIQUIDS/VAPOUR INTERFACE

The source of the the free energy existing in the boundary layer at a liquid/vapor interface results from the assymetry of forces around the molecules in or very near to the interface. Discontinuity in intensive physical properties such as densities is manifested when the boundary is traversed . The lattice model of the liquid was originally proposed by Frenkel (5). Here the spatial distribution of the nearest neighbours was assumed to be octahedral or in hexagonal close packing, as shown in the schematic below.

Here z is number of nearest neighbours in the bulk and z′ is the number of nearest neighbours of a surface molecule. For the octahedral case, one sixth of the lattice energy is unbalanced at the interface and $\frac{z-z'}{z} = \frac{1}{6}$, whereas for the hexagonal case one fourth of the lattice energy is unbalanced at the interface i.e. $\frac{z-z'}{z} = \frac{1}{4}$.



Frenkel related the latent heat of vaporization L to the energy of intermolecular forces per pair (u) of molecules by the following equation:

$$L = \frac{1}{2} \nu V z u \qquad \ldots . \quad (1.1)$$

ν = number of molecules per unit volume

V = molar volume

E^S = the total internal surface energy which is related to L as follows:

$$E^S = u (z-z') \nu^{2/3} \qquad \ldots . \quad (2.1)$$

$$= \frac{2L}{V} \left(\frac{z-z'}{z}\right) \nu^{-1/3} \qquad \ldots . \quad (3.1)$$

Definition of A

$$A^S = E^S - TS^S \qquad \ldots . \quad (4.1)$$

At constant pressure, TS^S is the enthalpy absorbed from the surroundings during the reversible extension of the surface. E^S is also the energy possessed by the surface molecules in excess of that which the same molecules would have in the bulk of the liquid. S^S is the excess surface entropy which is related to the surface tension of the pure liquid by the following:

$$S^S = \left(\frac{\partial A^S}{\partial T}\right)_{n_i,V} = -\left(\frac{\partial \gamma_O}{\partial T}\right)_{n_i,V} \qquad \ldots . \quad (5.1)$$

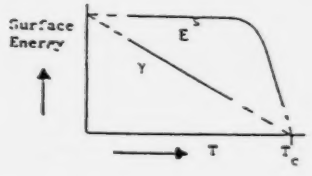
For a pure liquid with surface tension γ_o,

$$E^S = \gamma_o - T \left(\frac{\partial \gamma_o}{\partial T}\right)_{n_i,V} \quad \ldots . \quad (6.1)$$

and

$$\frac{\partial E^S}{\partial T} = \frac{\partial \gamma_o}{\partial T} - T \left(\frac{\partial^2 \gamma_o}{\partial T^2} \right) - \left(\frac{\partial \gamma_o}{\partial T}\right) = -T \frac{\partial^2 \gamma_o}{\partial T^2} \ldots . \quad (7.1)$$

As $\frac{\partial \gamma_o}{\partial T}$ is negative, $E^S > \gamma_o$, then since γ_o changes linearly with temperature and becomes zero at the critical temperature T_c, $\frac{\partial^2 \gamma_o}{\partial T^2} = 0$. E^S is independent of temperature, over a wide range and this is not so for surface tension γ, as is seen in the schematic below (5,8).



The above behaviour is most apparent in a sealed vessel or a closed system, where an interface separates a liquid from its vapour. The surface free energy which is equal to surface tension γ decreases linearly as temperature increases and approaches zero. At a critical temperature Tc the phase boundary disappears. At temperatures greater than Tc, the vapour could compress, yet the liquid phase would not separate. A positive surface free energy is required for forming a stable boundary, otherwise mixing takes place spontaneously.

The coordination number in Frenkel's model was replaced by a distribution function when the experimental latent heat of water did not agree with the calculated values (eqn.1.1). The Lennard-Jones 6/12 pair potential deduced for a pair of non-polar molecules (equation 8.1) replaced the pair bond energy of the Frenkel's model.

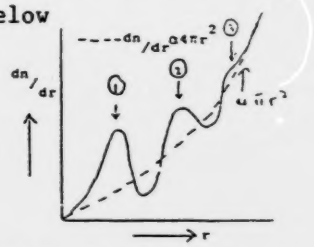
$$E^S = -Ar^{-6} + Br^{-12} \quad \ldots . \quad (8.1)$$

where A and B are constants and r is distance between pairs of molecules (5,8). Lennard-Jones showed that for Van-der-Waals molecules 80% of the total interaction was due to nearest neighbours. The distribution function in the surface region on the liquid side of the interface was the

same as in the interior of the liquid. It must be noted that the distribution about a given molecule in the surface region is made up of two parts, the molecules in the liquid phase and the molecules in the vapor phase. Usually if the concentration of molecules in the vapor phase is kept low by keeping the temperature low, the magnitude of interactions with the molecules in the gas phase would be small compared to the interactions in the liquid phases.

Jura (6) showed that a distribution function ,a potential function, and molal volume can be used to set up an equation for the surface energy of a liquid. He applied the expressions to liquid argon and mercury and found his calculated surface energies (32, 500 ergs cm^{-2}) were close to the observed values (35, 525 ergs cm^{-2})respectively. His conclusions was that 78% of the surface energy is derived from the first molecular layer, in the liquid and 99% of the surface energy came from interactions extending only to four molecular diameters of the surface, about 1.5 nm in depth. His expression for surface energy indicated that at low temperatures, the surface energy should vary with temperature in the same manner as the energy of vaporization. When the vapor pressure is low, the derivative of surface tension with respect to temperature should be zero.

More realistically, Kirkwood and Buff (7) developed a model using statistical mechanics. Surface tension was related to molecular distribution functions as well as potential intermolecular force (the Lennard-Jones pair potential). The derivative dn/dr represented the probability of finding a molecule at a distance r, from the centre of an arbitrarily chosen molecule as shown in the schematic below



Peaks 1), 2) and 3) correspond to the first, second and third nearest neighbours. They allowed suitable functions representing the density discontinuity across the interface to be used in their evaluation of surface tension and also surface "thickness", which is the distance δ separating the "surface of tension", distance r and Gibbs surface ($\Gamma_o = 0$). They calculated Argon at 90K to have $\gamma_o = 14.9\ mJm^{-2}$ and $E^S = 27.2\ mJm^{-2}$. Experimental values were 11.9 and 35 respectively. The δ was found to be 3.63A° which was close to the nearest neighbour peak of the radial distribution function (3.73A°). Their model lead to the conclusion that the surface tension of small

droplets decreases with increasing curvature. Their model is relatively insensitive to the previous distribution function for E (eq 8.1),(6).

To this day, further refinements of this model are hindered by lack of experimental information about the discontinuity limits at the interface. Rowlinson's model using molecular dynamics suggests that there is a periodic density near the interface. This was based on collision behaviour and Newton's laws of motion (8). Dabrowski et al (2) illustrates this discontinuity in their schematic of molecular distribution limits at the L/L and L/S interfaces Fig(1). Laplace has also attempted to show this by his model based on the pressure differences and radius of curvature at the interface (8,31). The Kelvin equation takes shape and curvatures into consideration in their calculation of surface tension based on pressure differences across the L/L, and L/V interfaces (9). These equations will not be pursued here for the sake of brevity. The reader is referred to reference 9 for further information..

In any event molecules in a liquid surface are in a constant state of exchange with the saturated vapour above it and the bulk liquid below the surface layer. Equilibrium is rapidly attained with liquids.

FOWKES'S MODEL OF THE LIQUID-LIQUID INTERFACE

In addition to the dispersion forces between molecules, contributions to surface energies and surface tension arise from many other interactions. These can be summarized as energies of interaction due to hydrogen bonding, metallic bonding, permanent dipole interaction and specific interactions. Between hydrocarbons, dispersion forces are the predominant interactive forces. In water, dispersion and hydrogen bonding contribute mainly to the measured interfacial tension value.

In the Fowkes' model the interface between two liquids 1,2, and their vapor 3 are described in the Figure (3). At the interface, between the hydrocarbon molecules 1 and water 2, the hydrocarbon molecules are attracted towards the bulk hydrocarbon phase, as well as attracted to the water molecules. The net attraction, is the geometric mean of the dispersion force components of the surface tensions of the hydrocarbon and water $(d_\gamma 1\ d_\gamma 2)^{1/2}$ The tension in the interfacial region of the hydrocarbon is $\gamma^{13} - (d_\gamma 1\ d_\gamma 2)^{1/2}$ and in the water phase $\gamma^{23} - (d_\gamma 1\ d_\gamma 2)^{1/2}$. The

measured interfacial tension is γ^{123} which is defined by the following equation:

$$\gamma^{123} = \gamma^{13} + \gamma^{23} - 2\,(d_\gamma 1\; d_\gamma 2)^{1/2} \quad \ldots \quad (9.1)$$

and

$$W_A^{123} = \gamma^{13} + \gamma^{23} - \gamma^{12} \quad \ldots \quad (10.1)$$

where W_A^{123} is the work required to separate unit area of the two surfaces and $2\,(d_\gamma 1\; d_\gamma 2)^{1/2}$ is the work of adhesion. Typical interfacial tension data are shown in Table 2. The Fowkes model is used in calculations of the surface tensions of liquids which cannot be measured directly. The work of adhesion indicates the extent of separation or miscibility of the liquids in contact with each other. This is useful in emulsion studies.

Measurement of Interfacial Tensions

In L/L and L/V systems there are a variety of techniques for directly measuring surface tensions. These are summarized with their advantages and disadvantages in Table 2. For solids, indirect determinations are made by contact angles between liquids of known γ and the surface of the solids (1,5,31). Recently two innovative methods, the solidification front or freezing front and the sedimentation volume techniques are being used for powders or solid samples that are unreactive with suspension liquids of specific γ (32,33).

The Structure and Energetics of Solid Surfaces

Normally most solids are not in stable thermodynamic equilibrium. In contrast to the mobility and uniformity of liquid surfaces, solid surfaces are immobile. Only limited regions on most solid surface would exhibit uniformity. Smoothness and homogeneity becomes relative depending on how close one looks at the surface. The surface of a solid is likely to have a wide range of surface free energies, which vary from region to region on the surface. Jaycock and Parfitt (9) have pointed out that if most solid geometries were of the minimum energy configuration, processes such as annealing and sintering would not occur. They also stated that the surface tension is not necessarily the same in all directions. This is especially so for anisotropic solids.

Surface stress is relieved, by deformation. This results in rows of dislocations just below the surface. The surface is stretched without increasing the area. In doing this, the surface energy as well as surface heterogeneity is increased. The surface would therefore exhibit a range of adsorption energies depending on the sites occupied by the adsorbed atoms or molecules. The energies required to form a range of population of different types of sites would vary in the same way as the range of population of different energetic sites.A heterogeneous surface as a result is likely to change with time if chemical interactions or annealing processes at the surface occur with time. In the case of a liquid, surface tension and surface stress are identical, whereas for a solid these differ. The surface tension for the solid is the excess free energy required to create a new surface in the equilibrium form.

The driving force for the reduction of surface areas in solids is greater than in liquids, because the surface free energies of solids are quite large. If the temperature is raised high enough to cause mobility in the solids, reduction of surface area follows, by spontaneous bridging of particles or coalescence of smaller particles. When sintering occurs,there is migration of material across the surface, which has a lower potential energy barrier than within the solids. Usually the temperature of sintering is around 0.5Tm, the melting point, usually called the Tamman temperature (8,9).The temperature of sintering is lowered by adsorption of impurities at the surface of the solid making surface migration easier. Populations of sites at equilibrium are "frozen-in" as the solid cools to room temperature. Deficiencies in crystals are formed in nucleation and crystallization processes as well.

Solids are also composed of functional group differences especially organic solids . Clays vary in composition, by exposure of broken edges, isomorphous substitution,lattice makeup. Bound extraneous materials on clays leaves further heterogeneity. Large variability in the solids and oxides formed are seen in modern day Scanning Electron micrographs of materials in catalysis, metallurgy, polymer synthesis and mineralogy. Differences in the adsorptive behaviour of homogeneous and heterogenous solids are mainly due to large differences in surface energies. surface areas, and functional group makeup. Kipling (1) illustrated this selectivity in adsorption

differences on Spheron (heterogenous) and Graphon (homogeneous) carbon based solids.

MODELS OF ADSORPTION- THERMODYNAMICS AT THE INTERFACE

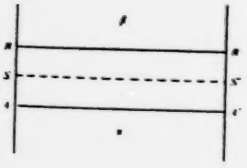
THE GIBBS SURFACE EXCESS

Young (1805) and Gibbs (1872) originated the basic fundamental concepts of surface chemistry. Young's "surface" was described by mechanical properties and together with Laplace described surface tension in terms of pressure and geometry (9). Gibbs, was responsible for the famous "Gibbs dividing surface" and hence the "excess surface properties", which in terms of surface concentration was the extent by which a specie at the surface exceed the same specie in the bulk. The Gibbs dividing mathematical plane between two phases, however, did not account for molecular dimensions within the interfacial region. The Gibbs adsorption isotherm made no assumptions for the nature of the adsorbing process. It was used as a means of measuring adsorption at the L/V interface from surface tension data. All this happened before the advent of polymers or the quantitative techniques for determining molecules at a surface, ie. before spectroscopy and ellipsometry (9).

To this day many researchers find it convenient to use the Gibbs surface. Purposely defining a dividing plane with zero excess quantities of one component, simplifies matters in a multicomponent system. The general Gibbs treatment considers a multicomponent two-phase system of known volume V, with phases α and β, shown in the schematic below. The Gibbs dividing surface SS′ separates these phases, and the bulk concentration of all components are assumed to be unchanged right up to the interface where they undergo a step-change (Figs.1,2). For a total n_i moles of species i in the system, $n_i = n_i^{\alpha} + n_i^{\beta} + n_i^{\sigma}$. Here n_i^{α}, n_i^{β}, and n_i^{σ} are the number of moles i in phases α, β and in the dividing plane σ. The surface excess concentration is then defined as:

$$\Gamma_i^{\sigma} = \frac{n_i - n_i^{\alpha} - n_i^{\beta}}{a} \qquad \ldots . \quad (11.1)$$

where Γ_i^σ, is the surface excess concentration and 'a' is area of the interface. Thus surface excess concentration Γ^σ is the adsorption per unit area of the Gibbs dividing surface. This is better visualized in the schematic below (3,19).



$$\Gamma_i^\sigma = \frac{n_i - n_i^\alpha - n_i^\beta}{a} = \frac{n_i^\sigma}{a} \quad \ldots\ldots \quad (12.1)$$

$$= \frac{n_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta}{a} \quad \ldots\ldots \quad (13.1)$$

$$\Gamma_i^\sigma = \frac{n_i - c_i^\alpha V + (c_i^\alpha - c_i^\beta)V^\beta}{a} \quad \ldots\ldots \quad (14.1)$$

c_i^α and c_i^β are molar concentrations of component i in the phases α and β respectively, and V is the volume of the system. V^β and V^α are the phase volumes($V = V^\alpha + V^\beta$) . The position of the interface must be clearly defined since a small displacement ΔL in the position of the interface changes the surface excess concentrations, as seen in 15.1.

$$\Delta\Gamma^\sigma = (c_i^\alpha - c_i^\beta)\Delta L \quad \ldots\ldots \quad (15.1)$$

For two components such as solute 2 and solvent 1,usually ,if V and the adsorption of one component is known,and the solvent 1 is chosen to be zero then:

$$\Gamma_1^\sigma = 0 = \frac{n_1 - c_1^\alpha V + (c_1^\alpha - c_1^\beta)V^\beta}{a} \quad \ldots\ldots \quad (16.1)$$

and

$$V^\beta = \frac{c_1^\alpha V - n_1}{c_1^\alpha - c_1^\beta} \quad \ldots\ldots \quad (17.1)$$

Fixing the position of the interface,thus V^β is defined in terms of known quantities. When V^β in 17.1 is substituted in 14.1 and 16.1 the surface excess concentration in the Gibb's dividing surface σ is related to solvent adsorption by 18.1.

$$\Gamma_i^{\sigma} - \frac{c_i^{\alpha} - c_i^{\beta}}{c_1^{\alpha} - c_1^{\beta}} \Gamma_1^{\sigma} = \Gamma_i^{(1)} \qquad \ldots . \quad (18.1)$$

where $\Gamma_i^{(1)}$ is the relative surface excess concentration of i species. If α is considered to be a gas phase, then $c_1^{\alpha} \sim c_i^{\alpha}$ is negligible and the relative surface excess concentration from equation 14.1 and 18.1 is:

$$\Gamma_i^{(1)} = \frac{1}{a} \left(n_i - c_i^{\beta} V^{\beta} \right) \qquad \ldots . \quad (19.1)$$

When the interphase is considered, there is interfacial thickness. More realistically, Guggenheim defined the interfacial layer bounded by two dividing planes which were situated in the homogeneous parts of α and β respectively. The interphase had a finite thickness t and volume V^S is treated as follows.

$$V^S = ta \qquad \ldots . \quad (20.1)$$

$$\Gamma_i^S = \frac{1}{a} \left(n_i - n_i^{\alpha} - n_i^{\beta} \right) \qquad \ldots . \quad (21.1)$$

$$= \frac{1}{a} \left(n_i - c_i^{\alpha} V^{\alpha} - c_i^{\beta} V^{\beta} \right) \qquad \ldots . \quad (22.1)$$

$$V = V^{\alpha} + V^{\beta} + V^S \qquad \ldots . \quad (23.1)$$

For liquid-liquid systems, the Guggenheim treatment becomes more complicated.

Guggenheim Versus Gibbs Treatment

In the past, adsorption received a great deal of attention because of the wide applications and has been the subject of many review articles and books. Kipling (1965) addressed adsorption isotherms from a practical point of view in a comprehensive survey (1). Schay has qualitatively classified adsorption isotherms from adsorption data of miscible liquids onto solids. These qualitative composite isotherms were U-type, S-type,and linear Fig.(4). Schay also reviewed comprehensively adsorption of low molecular weight solutes at L/V and S/V interfaces (10). Although

'preferential' adsorption was the term used historically, to describe adsorption of liquids onto solids and Gibbs Excess for L/L or L/V interfaces, today the Gibbs Excess is applied to both systems.

With the extensive use of the Gibb's equation for surface excesses, came many misunderstandings associated with its uses. In a treatise of the thermodynamics of adsorption at the surface of solutions,Guggenheim and Adam (11) have clearly stated that there is some confusion in interpreting the results of Γ, in terms of the physical structure of the surface. The Gibbs convention also suffers the disadvantage that it is not easily visualised in terms of the physical structure of the surfaces. Surfaces possess an assymmetrical nature with respect to the adsorbing solution, yet the Gibbs model disregards this. The two bulk phases are considered to be completely homogeneous except in the immediate neighbourhood of the surface. Gibbs chose the position of the geometric surface such that for one component 1 the value Γ_1 is zero. Discussion of the surface excess is normally confined to systems of two bulk phases in complete thermodynamic equilibrium separated by a plane surface. For curved surfaces, the choice of the dividing surface is very unlikely to coincide with the surface of tension, leaving a model system not mechanically equivalent to the real one.

Guggenheim and Adam cited five alternative conventions for fixing the values of $\Gamma_i^{(\ )}$. These are

$\Gamma_1^{(1)}$ - standard Gibb's convention $\Gamma_i^{(1)}=0$

$\Gamma_2^{(2)}$ - where Γ_1 is the excess number of moles of species i in a portion of the liquid with unit surface area, over a portion in the bulk containing exactly the same number of moles of species 2 ($\Gamma_2^{(2)}=0$).

$\Gamma_i^{(N)}$ - a liquid portion of unit area with Γ_i moles of species i over the bulk with same number of moles of all species $\sum_i \Gamma_i^{(N)} = 0$

$\Gamma_i^{(m)}$ - a liquid portion of unit area with Γ_i moles of species i over a bulk portion of same mass. $\Sigma m_i \Gamma_i^{(m)} = 0$

$\Gamma_i^{(V)}$ - a liquid portion of unit area with Γ_i moles of species i over a portion of bulk with same volume $\sum_i V_i \Gamma_i^{(V)} = 0$

The arguments are that $\Gamma_i^{(V)}$ relations are often used in situations which are exact only for the $\Gamma_i^{(1)}$. The last convention is the only one where the geometric surface co-incides with the physical boundary of the liquid. If two species are of comparable molar mass and molar volume it

will approximate for $\Gamma_i^{(N)}$ and $\Gamma_i^{(m)}$. However, $\Gamma_2^{(1)}$ and $\Gamma_1^{(2)}$ can be related to $\Gamma_i^{(N)}$ $\Gamma_i^{(m)}$ and $\Gamma_i^{(V)}$. Further details on these relationships are seen in references 1 and 11. Goodrich (12) and Schay (10) independently, were also critical of the Gibb's dividing plane and showed by a method of algebraic multipliers that the volume of the surface phase can be included in Γ.

Common to L/L, L/V and L/S interfaces are interpretations and modifications of the models and theories used to explain experimental results. Kipling devoted an entire text to the qualitative and interpretive aspects of adsorption from solutions of nonelectrolytes (1). The following relationships were devised for a two component system(1,11),:

$$\Gamma_2^{(N)} = X_1 \Gamma_2^{(1)} = \frac{M}{M_1} \Gamma_2^{(m)} = \frac{V}{V_1} \Gamma_2^{(V)} \quad \ldots . \quad (24.1)$$

where V_1, and V are the partial molar volume of component 1 and the mean molar volume of the solution respectively. M_1 and M_2 are the molecular weights of components 1 and 2 respectively and M the mean molecular weights of the solution. When L/V and L/S interfaces are compared,

$$-\Gamma_2^{(N)} = \Gamma_1^{(1)} = -\frac{n_o \Delta x}{Sm} \quad \ldots . \quad (25.1)$$

m is the mass of solid added to n_o moles of liquid and Δx is the decrease in mole fraction of the liquid with respect to component 1. S is the specific surface area of the solid.

The Gibbs equation nevertheless is the most widely used in the study of monolayers (13), surfactants (14), electrolyte adsorption (15). The thermodynamics of excesses still remains one of the most rigorous modes of description of the interface. It has great utility in experimental studies.

Ikeda (16) presented a comprehensive review of the applications of the Gibb's adsorption isotherm for aqueous electrolyte solutions. Chattoraj and Birdi have devoted an entire text to the Gibb's surface excess (17). However the relationship between the Gibbs free energy function G or the Helmholtz free energy or work function A with Γ_i^S or Γ_i^σ is best expressed through classical thermodynamics.

Derivation of the Gibbs Equation

This section will present the classical thermodynamics for bulk liquids, with the variations used to describe the surface properties in a planar interface. The intention is to show how the famous Gibbs equation was developed from classical thermodynamics.

In a closed system, if surface effects are neglected the internal energy E is defined by the first law of thermodynamics

$$E = Q + W \quad \ldots . \quad (1.2)$$

$$dE = DQ + DW \quad \ldots . \quad (2.2)$$

where DQ is the heat taken up by the system for an infinitesimal change and DW is the work done on the system. At equilibrium the infinitesimal change is reversible and if the work done is only associated with volume change then

$$DW = -pdV \quad \ldots . \quad (3.2)$$

where V is the volume and p is the pressure of the system.From the second law of thermodynamic DQ= TdS

where S is entropy and T the temperature of the system

$$dE = TdS - pdV \quad \ldots . \quad (4.2)$$

If the system is open, then

$$dE = TdS - pdV + \Sigma_i \mu_i dn_i \quad \ldots . \quad (5.2)$$

where μ_i is the chemical potential of component i and n_i the number of moles of i in the system, Σ_i refers to the sum of all species 1,.i in the system.

If the system has an interface, the work done may change the area of the interface as well as the volume of the adjacent bulk phases and is,

$$DW = -pdV + \gamma da \quad \ldots . \quad (6.2)$$

Here γ is the interfacial tension and 'a' is the interfacial area. If we assume that the interface is in equilibrium with the bulk, μ_i would be the same in all phases. Internal energy of the system is then,

$$dE = TdS - pdV + \sum_{\sigma} \mu_i dn_i + \gamma da \quad \ldots . \quad (7.2)$$

For the surface or interface if $dV=0$, then

$$dE^{\sigma} = TdS^{\sigma} + \gamma da + \sum_{i} \mu_i dn_i^{\sigma} \ldots . \quad (8.2)$$

Here γda is positive and an increase in area a increases the energy of the system. In the case of a gas where dV is significant an increase in V diminishes the energy of the system. When (7.2) is integrated between limits zero and σ surface, then

$$E^{\sigma} = TS^{\sigma} + \gamma a + \sum_{i} \mu_i n_i^{\sigma} \quad (9.2)$$

Differentiating (9.2) and equating it to (8.2) gives (10.2)

$$0 = S^{\sigma} dT + a d\gamma + \sum_{i} n^{\sigma} d\mu_i \quad (10.2)$$

At constant T, and substituting $\Gamma_i = n_i^{\sigma}/a$, we get (12.2),and

$$0 = a d\gamma + \sum_{i} n_i^{\sigma} d\mu_i \quad (11.2)$$

$$-d\gamma = \sum_{i} (n_i^{\sigma}/a)\, d\mu_i = \sum_{i} \Gamma_i d\mu_i \quad (12.2)$$

Equation (10.2) represents the equilibrium form for the surface phase. The chemical potential μ_i of specie i must be the same for the component i in all phases at equilibrium with one another. Equation (12.2) relates an increment in chemical potential of the surface active specie i in the solution to a decrease in the surface tension, which can be measured. The surface excess Γ_i was derived previously. Equation (12.2) is one form of the Gibbs equation.The Helmholtz function A for the surface is defined by:

$$A^{\sigma} = E^{\sigma} - TS^{\sigma} \quad \ldots . \quad (13.2)$$

$$dA^{\sigma} = dE^{\sigma} - TdS^{\sigma} - S^{\sigma} dT \quad \ldots . \quad (14.2)$$

$$E = E^{\sigma} + E^{\alpha} + E^{\beta} \qquad (15.2)$$

$$G = G^{\sigma} + G^{\alpha} + G^{\beta} \qquad (16.2)$$

Substituting 8.2 for dE^{σ} in 14.2, we get:

$$dA^{\sigma} = TdS^{\sigma} - pdV^{\sigma} + \gamma da + \sum_i \mu_i dn_i^{\sigma} \quad .... \quad (17.2)$$
$$-TdS^{\sigma} - S^{\sigma}dT$$

$$dA^{\sigma} = -S^{\sigma}dT - pdV^{\sigma} + \gamma da + \sum_i \mu_i dn_i^{\sigma} \quad .... \quad (14.2)$$

If we consider the whole system, then

$$dA = -SdT - pdV + \gamma da + \sum_i \mu_i dn_i \quad .... \quad (15.2)$$

When T, P, μ_i and γ which are intensive properties are held constant, and equation (15.2) is integrated between zero and σ we get (16.2):

$$A^{\sigma} = -pV^{\sigma} + \gamma a + \sum_i \mu_i dn_i^{\sigma} \quad .... \quad (16.2)$$

Again γ can be related to the Helmholtz work function A^{σ} in 16.2 .and similarly the Gibbs free energy G^{σ}can also be defined in terms of the interfacial tension by suitable manipulations of the basic definition for G in terms of E,P,T,S to give:

$$G^{\sigma} = \gamma a + \Sigma \mu_i \Gamma_i^{\sigma} \qquad (17.2)$$

γ is therefore shown to be the isothermal work done in extending the interface by unit area, at constant V and n_i. Other excess relationships have been derived to give the following Maxwell analogs (19).

$$\gamma = \left(\frac{\partial H^{\sigma}}{\partial a}\right)_{S,P,n_i} \qquad \gamma = \left(\frac{\partial A^{\sigma}}{\partial a}\right)_{T,\ V^{\sigma},n_i^{\sigma}} \quad .... \quad (18.2)$$

$$\gamma = \left(\frac{\partial E^{\sigma}}{\partial a}\right)_{S,V,n_i} \qquad \gamma = \left(\frac{\partial A}{\partial a}\right)_{T,\ V,\ n_i} \quad .... \quad (19.2)$$

When there is no adsorption, γ is the specific excess surface free energy. However, most times $\sum_i \mu_i \Gamma_i^{\sigma} \neq 0$. When using the Guggenheim approach $V^S \neq 0$

$$G_s = \gamma + \sum_i \mu_i \Gamma_i^S \quad .... \quad (20.2)$$

Where s is the interfacial phase. G_s is then the specific total surface free energy and Γ_i^s is total surface concentration. In this case $\sum_i \mu_i \Gamma_i^s$ is never zero even for pure liquids, and G_s is not equal γ.
Surface chemical potentials are also defined as:

$$\mu_i^\sigma = \left(\frac{\partial A^\sigma}{\partial n_i^\sigma}\right)_{T,\ V,\ n_j^\sigma,a} \qquad \ldots\ldots \quad (21.2)$$

If the surface is in equilibrium with the bulk, then

$$\mu_i = \mu_i^\sigma \qquad \ldots\ldots \quad (22.2)$$

If no concentration change results from the addition of material, then the free energy change is independent of the phases α, β or s to which the material is added. In terms of the Gibbs function, the chemical potential is the partial molar Gibbs free energy and can be expressed as:

$$\mu_i^\sigma = \left(\frac{\partial G^\sigma}{\partial n_i^\sigma}\right)_{T,\ P,\ n_j^\sigma a} \qquad \ldots\ldots \quad (23.2)$$

The interfacial tension γ changes when adsorption takes place. The Gibbs adsorption equation is thus a thermodynamic expression which relates the surface concentration (surface excess) to γ and bulk activity or fugacity of the adsorbate. Surface concentrations of L/L and L/V systems can be determined directly through γ. On other system where γ cannot be measured directly but concentrations can be measured, the Gibbs equation is used to calculate the lowering of γ. This decrease is called the spreading pressure π, ($\pi = \gamma_o - \gamma$) in solid/gas systems. In the Gibbs approach all the extensive thermodynamic properties of the surface are defined as excess rather than total quantities.
The equation (12.2) is the general form of the Gibb's equation. In the Gibb's sense Γ_i is the surface excess of component i, and in the Guggenheim sense Γ_i is the surface concentration of component i.

In the simplest case of a two component system in which (1) is the solvent and (2) is the solute, or a two component liquid mixture at the liquid-vapour interface, then:

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \qquad \ldots\ldots \quad (24.2)$$

If the Gibb's dividing surface is S'-S' as in Figure (2), then $\Gamma_1 = 0$ and

$$-d\gamma = \Gamma_2^{(1)}\, d\mu_2 \qquad \ldots . \quad (25.2)$$

where $\Gamma_2^{(1)}$ is the relative adsorption of component 2 with respect to component 1. If we recall in the bulk phase that

$$\mu_2 = \mu_2^o + RT \ln a_2 \qquad \ldots . \quad (26.2)$$

where μ_2^o is the standard chemical potential of component 2 and a_2 the activity of the solute 2. Differentiating (26.2) gives (27.2):

$$d\mu_2 = RTd\ln a_2 \qquad \ldots . \quad (27.2)$$

substituting (27.2) in (25.2) gives (28.2):

$$\Gamma_2^{(1)} = -\frac{1}{RT}\,\frac{d\gamma}{d\ln a_2} \qquad \ldots . \quad (28.2)$$

If the Guggenheim approach of the surface phase model is used and the surface is assumed to have a finite thickness, then Γ_1 and Γ_2 which are total surface concentrations, are written Γ_1^s, Γ_2^s respectively.

At equilibrium μ_1 and μ_2 are the same in all phases. For a bulk phase at constant temperature and pressure, the Gibbs-Duhem equation (29.2) indicates that the chemical potentials of all components are related to each other as follows:

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \qquad \ldots . \quad (29.2)$$

in terms of mole fractions:

$$X_1\, d\mu_1 + X_2 d\mu_2 = 0 \qquad \ldots . \quad (30.2)$$

$$X_1\, d\mu_1 = -X_2 d\mu_2 \qquad \ldots . \quad (31.2)$$

Since from (24.2) $\quad -d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \ldots \qquad \ldots . \quad (32.2)$

Then $d\mu_1$ from (31.2) into (32.2)gives (33.2) :

$$-d\gamma = [\Gamma_2^s - \frac{X_2}{X_1}\Gamma_1^s]\, d\mu_2 \ldots \qquad (33.2)$$

then $d\mu_2$ from (27.2) in (33.2) gives:

$$\Gamma_2^s - \frac{X_2}{X_1}\Gamma_1^s = -\frac{1}{RT}\,\frac{d\gamma}{d\ln a_2} \qquad \ldots . \quad (34.2)$$

The bracketed terms of (33.2) is equivalent to $\Gamma_2^{(1)}$ of the Gibb's model. This is also independent of the positions of the planes AA'and BB'of Figure (1).Therefore :

$$\Gamma_2^{(1)} = \Gamma_2^s - \frac{X_2}{X_1} \Gamma_1^s \qquad \ldots . \quad (35.2)$$

Eq (35.2) means that $\Gamma_2^{(1)}$is a surface excess concentration of 2 per unit area of surface minus the number of moles of 2 in that part of the bulk region which contains the same number of moles of 1, third term in (35.2). In very dilute systems $\frac{X_2}{X_1}\Gamma_1^s$ is negligible compared to Γ_2^s so that $\Gamma_2^{(1)}$ is about equal to $\Gamma_2^{(s)}$.

In practice it is difficult to assign values to Γ_1^s and Γ_2^s. Sometimes the surface phase is assumed to have a monomolecular layer, and

$$\Gamma_1^s a_1 + \Gamma_2^s a_2 = 1 \qquad \ldots . \quad (36.2)$$

in which a_1 and a_2 are the partial molar surface areas of components 1 and 2 respectively, and are assumed to be constant.

Written in terms of concentration and in a general form, the Gibbs equation becomes:

$$\Gamma_i^{(1)} = - \frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln c_i}\right)_{T,c, \ldots . c_{i-1}} \qquad \ldots . \quad (37.2)$$

Where:

$\Gamma_1^{(1)}$ = surface excess of component i relative to component 1.

R = universal gas constant

T = absolute temperature

γ = surface tension

c_i = bulk concentration of component i

c_i could be replaced by activity, or mole fractions, provided the same is used in the definition of standard state.

For a comparison of different interfaces, the $\Gamma_i^{(N)}$ convention of Guggenheim is used. For two component system:

$$\Gamma_2^{(N)} = - \frac{X_1 \, d\gamma}{RT d \ln a_2}$$

If the vapours of the two components obey the perfect gas laws

$$\Gamma_2^{(N)} = - \frac{X_1 \, d\gamma}{RTd\ln p}$$

Other definitions are

$$\Gamma_2^{(m)} = - \frac{M_1 X_1 \, d\gamma}{M_2 RTd\ln a_2}$$

$$\Gamma_2^{(V)} = - \frac{V_1 X_1 \, d\gamma}{V RTd\ln a_2}$$

The convention one uses would reflect the experimental design. If interest is in adsorption mechanisms, energetics of adsorption would only provide the limiting values by which any mechanism must be consistent. However, if simplicity and generality is sought, the Gibbs equation is most suitable. Adsorption at the L/V and L/L interface occur in processes such as emulsion stabilization, wetting, enhanced oil recovery, microemulsion formation (13). In all cases positive adsorption leads to lowering of the interfacial tension and vice versa.

Recently published work by Ghosh et al (15) showed the opposite. Electrolytes caused the increase in surface tension at the air/water and oil/water interfaces, due to negative adsorption. The standard free energies of negative adsorption calculated for the electrolytes at different interfaces were all positive.

Critique on Adsorption at the Solid/Liquid Interface

Previously the solid structure and the variation of high energies and low energy sites were discussed. In addition the solid surface may be highly charged due to surface functional group exposure or lattice deficiencies. Altogether the solid surface in broad terms may be hydrophilic (high energy) or hydrophobic (low energy) or a combination of both depending on the material. The state of the surface can be critically dependent on the solution conditions such as pH, electrolyte, temperature, and sorbate. There is thus no unified general approach to studying adsorption at the solid/liquid interface.

The detailed and comprehensive review of adsorption from liquid mixtures of non-electrolytes on solid surfaces recently published by

Dabrowski et al (2), suggested that progress in liquid adsorption processes have not received as much attention as solid-gas adsorption, although the former has wide practical applications. They claimed that the theoretical studies are divided into two groups,which are,classical (A) and statistical(B). A) In the classical sense,the theoretical studies dealing with liquid adsorption are based on the assumptions of: 1. the existence of surface and bulk phases, 2. molecular sizes of components forming a liquid mixture are similar, 3. chemical equilibrium exist between the two phases, 4. the surface phase has a monomolecular layer and 5. no interactions occur between bulk and surface.

Other theories(B) are based on a full statistical thermodynamic description of adsorption at the solid/liquid interface. These include molecular dimensions. Polymer adsorption falls into this group. Concentration as a function of distance from the solid surface can be calculated, as well as orientation of adsorbed molecules at the interface can be established. The intermolecular forces acting at the interface of these systems are difficult to determine since the traditional theory was developed only for simple systems. The Polyani theory (3) though was successful in describing adsorption from liquid mixtures with incomplete miscibility (4).

Schay reviewed the fundamental thermodynamic properties of adsorption from binary liquid mixtures of nonelectrolytes (10) at L/S, L/V interfaces, and chose the idealized monolayer surface phase model.Some similarities was drawn between adsorption at these different interfaces. However, as was pointed out by Dabrowski et al (2) and earlier by Kipling (1), the monolayer model is thermodynamically inconsistent and is often incompatible with experimental data.

Multilayer adsorption from solutions of nonelectrolytes on solids also present many problems . Dabrowski's assumptions in his discussions on liquid adsorption for both heterogeneous and homogeneous surfaces are

(1) no chemical reactions occur between solution and solids
(2) the solid surface is accessible equally to all components of the solution and molecular sieves effects are excluded
(3) all proportions of mixtures can be considered.

The excess thermodynamic function, was generalised by

$$Y^{\sigma} = Y - n^{\alpha} Y_m^{\alpha} - n^{\beta} Y_m^{\beta} \quad \ldots . \quad (1.3)$$

Y expressed, either as internal energy, enthalpy or entropy. His equation (2.3) defines n_i^1 as number of moles in the bulk liquid phase:

$$\sum_i n_i^{\sigma(n)} = \Sigma_i (n_i - n^1 x_i^1) = 0 \quad \ldots . \quad (2.3)$$

It reflects that liquid adsorption is competitive. The chemical potential which characterizes the state of adsorbed molecules in the surface phase is

$$\mu_i^s = \left(\frac{\partial A}{\partial n_i^s}\right)_{T,V^s,\, a_s,\, n_j^s \neq i} \quad \ldots . \quad (3.3)$$

$$= \mu_i^o + RT \ln (f_i^s x_i^s) + (\gamma_i^o - \gamma) a_i \quad \ldots . \quad (4.3)$$

Here μ^o is the chemical potential of the ith pure liquid, f_i is the activity coefficient of the ith component in the adsorbed phase, γ_i^o is the interfacial tension at the solid/ith pure liquid interface, and γ is the interfacial tension at the S/L interface. One can define a_i by

$$a_i = a_i^o / t \quad \ldots . \quad (5.3)$$

where a_i^o is the molar cross-sectional area of the ith component, a_i is the partial molar area of ith component, and t is a constant for thickness of adsorbed phase in the monolayer model described by Everett (18).

$$a_i = \left(\frac{\partial a_s}{\partial n_i^s}\right)_{T,V^s,\sigma,\, n_j^s \neq i} \quad \ldots . \quad (6.3)$$

$$\gamma = \left(\frac{\partial A}{\partial a_s}\right)_{T,V^s,\, n_j^s} \quad \ldots . \quad (7.3)$$

$$d\gamma = -\sum_{i \neq 1} \Gamma_i^{(1)}\, d\mu_i = -\sum_{i \neq 1} \Gamma_i^{(n)} d\mu_i / (1 - x_i^1) \quad \ldots . \quad (8.3)$$

Activity coefficient at the surface phase or surface activity coefficent was defined as follows:

$$f_i^s = (x_i^l \, f_i^l / x_i^s) \exp[(\gamma - \gamma_i^o) \, a_i / RT] \quad \ldots . \quad (9.3)$$

f_i^l = bulk activity coefficient.

μ_i^s is also a function of surface phase composition.

$f_i^s = 1$ as $x_i^l = 1$

Also distribution coefficient was described as:

$$\alpha_{12} = (x_1^s \, x_2^l) \, / \, (x_2^s \, x_1^l) \quad \ldots . \quad (10.3)$$

If there was positive adsorption of the first component $\alpha_{12} > 1$, and if there was positive adsorption of the second component then $\alpha_{12} < 1$.

For heterogeneous surfaces two models are often used in adsorption,

1) The patchwise model (PM), where the adsorption sites are of equal energies. The sites are grouped in patches, and the patches are large so that interaction between two molecules adsorbed on the patches are neglected.
2) The random model (RM), where the sites of equal adsorption energies are assumed to be randomly distributed over the heterogeneous surface.

In the latter case a distribution function is used. This allows study of the nature of the heterogeneity effects in solid/liquid systems. It cannot be used to compare with gas adsorption and liquid adsorption.

Experimental Methods For Studying Adsorption

Experimental methods used for studying adsorption on to solids from solutions include:

1) Measuring adsorption over wide concentration and temperature ranges, by interfacial tensions.
2) Measuring heats of immersion first of solids in pure liquids and then in mixtures.
3) Measuring density changes of the sorbate-sorbent complex.
4) Spectroscopy

The nature of heterogeneity effects in solid/liquid systems proposed by Aveyard and Haydon, could be studied by using the excess isotherm for L/V and L/L homogeneous surfaces and comparing them to S/L interfaces. For further details on adsorption models, references (1,2) can be consulted. The applications of method 1 is shown in the section on temperature dependence studies to follow. Method 2 is elaborated next with respect to heat capacities. Heats of adsorption can be related to the surface tension through immersion experiments in calorimetry.

Surface Tensions from Heats of Solutions

If the heats of immersion of large crystals are measured, surface effects are often ignored (19). Then

$$H_{large} = TS_{large} \quad \ldots . \quad (1.4)$$

where H_{large} is the heat of solution per gram of large crystals, S_{large} is entropy of solution of large crystals, T is the absolute temperature. For small crystals

$$H_{small} = TS_{small} + \gamma A \quad \ldots . \quad (2.4)$$

where

a = area per gram of material

γ = surface tension

Surface excess enthalpy $h_s = TS_s + \gamma$ . . . . (3.4)

h_s = surface excess enthalpy per unit surface area

h_s $$h_s = \frac{H_{small} - H_{large}}{a} \quad \ldots . \quad (4.4)$$

S_s = surface excess entropy per unit area and is

$$S_s = \frac{S_{small} - S_{large}}{a} \quad \ldots . \quad (5.4)$$

Therefore if the heats of solutions of large and small crystals of known surface areas are known, surface tension can be determined, by measuring the heats of solution as a function of temperature and by extrapolation. Using heat capacity differences of coarse and fine particles.

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \qquad \ldots . \quad (6.4)$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \ldots . \quad (7.4)$$

$$h_{s,T} = h_{s(298)} + \frac{1}{a}\int_{298}^{T} \Delta C_p dT \cdot \ldots \quad (8.4)$$

$$S_s = \frac{1}{a}\int_{o}^{T} \frac{\Delta C_p}{T}\, dT \qquad \ldots . \quad (9.4)$$

The surface excess enthalpy (h_s) and surface excess entropy (S_s) can be calculated. Although in theory this seems like an easy way of determining the surface tension of fine particles of the same material, it is not an easy experiment to perform. Ignoring the surface tension in the large particles of the same material, would depend on hov large a size one is considering. Also the relative heterogeneity of the material may be a large source of error. Relative porosities would also present some problems.

Surface excess entropy of adsorption and the temperature dependence have been studied for a variety of systems. Complete thermodynamic characterization of adsorption requires enthalpy, entropy,and free energy data (18). These may be obtained by either temperature dependence studies or by direct calorimetry. Studies in temperature dependence are reviewed in the following section.

PART II TEMPERATURE DEPENDENCE

ADSORPTION, SURFACE TENSION AND TEMPERATURE DEPENDENCE

The effects of temperature on surface thermodynamics are sparsely studied in the literature. The following survey projects the diverse areas

in which surface thermodynamics and temperature increases or decreases have been researched in the past.

As early as 1965, Kipling noted that temperature affected several factors which were important in adsorption from solution. He showed that for completely miscible systems such as ethylene dichloride and benzene, or methyl acetate and benzene selective adsorption on alumina (boehmite) decreased with temperature rise. This is expected in exothermic processes. As temperature rose, a decrease in preferential adsorption of acetic acid aqueous solutions on charcoal was observed. A polar solid showed more marked differential effects with adsorption of less polar liquid mixtures, when temperature was increased (Fig. 5). On silica gel temperature had no effect on selective adsorption of benzene-ethyl alcohol mixtures and this was attributed to chemisorption, by the silica gel.

From completely miscible liquids, selectivity decreased with temperature rise. As temperature decreased, and as the critical temperature was approached, multilayer adsorption was likely to occur.

For solutions of solids or liquids of limited miscibility, increase in temperature reduced selectivity. Increased solubility due to temperature rise would result in increased adsorption in some cases. Decreased solubility with temperature rise would have the opposite effect.

From the Gibb's equation one can predict that γ would decrease as T is increased. If the following analogue of the Gibbs-Duhem equation is examined,

$$d\gamma = -S^{\sigma}dT - \sum_i \Gamma_i \, d\mu_i \qquad \ldots . \quad (1.5)$$

it can be seen that at constant T, and P the surface tension is varied by the variation in composition at the surface. If however T is varied, then the change in surface tension is influenced by the surface chemical potential and surface entropy. In any event an increase in surface entropy leads to a decrease in surface tension. Variation of surface tension with temperature can be related to the excess internal energy per unit area of the surface by the Guggenheim-Goodrich equation (refs. 5,8) below:

$$E^S = \gamma - T \left(\frac{d\gamma}{dT}\right)_a = E - \Gamma^1 \times E_1 \qquad \ldots . \quad (2.5)$$

where

E^S is internal energy of the molecules in the surface region,

Γ^1 is the total number of molecules in the surface region,

E_1 is internal energy for a molecule in the bulk phase.
E is internal energy of the whole system.

From $d\gamma/dT$ surface entropy S^S and surface internal energy E^S can be calculated. Complete thermodynamic characterization are obtained either by temperature dependence studies or by direct calorimetry (18). Everett showed how changes in surface tension with temperature can be used together with heats of wetting to determine surface enthalpy. Other experimental and theoretical work in the past has led to several empirical equations relating surface tension with temperature. These are considered as classic and are used frequently in metallurgy. The Eotvos equation was an experimental relationship established for surface tension of a liquid in equilibrium with the vapour. γ was calculated for different liquids with the Ramsay-Shields formula (5).

1) Eotvos: $$\gamma(Vm)^{2/3} = k(Tc-T) \quad \ldots . \quad (3.5)$$

where Vm is the molar volume, Tc the critical temperature, K is a constant.

(2) Van der Waals: $$\gamma = \gamma o(1-T/Tc)^{1.23} \quad \ldots . \quad (4.5)$$

$$K = \frac{\gamma o(1-T/Tc)^{0.23}}{Tc\,Vm^{-2/3}} \quad \ldots . \quad (5.5)$$

Here γo is a constant independent of temperature, the surface tension at 0 Kelvin. These work well for nonpolar liquids.

In addition there are other empirical linear relationships established for determination of surface entropy $(-\frac{\partial\gamma}{\partial T})$ or temperature coefficient. Kasama et al (20) have used the oscillating drop method to study the temperature dependence of surface tension of liquid copper. Again a linear relationship after least squares analysis was found

$$\gamma = 1382 - 0.27(T-1356) \quad \ldots . \quad (6.5)$$

where 1382 is the value of γ (mNm^{-1}) at the melting point 1356K. Temperature coefficients of others for liquid copper showed the following:

$$-0.33 < d\gamma/dT < -0.21 \text{ (Kasama et al)}$$

$$-0.49 < d\gamma/dT < -0.37 \quad \text{(Soda et al)}$$

They claimed that the temperature coefficient of γ for copper changes from negative to positive with increasing surface active impurities such as oxygen, since older literature values were all positive.

The Kirkwood and Buff (7,20) theoretical equations for surface tensions from interatomic potential and pair correlation functions (previously described) depend on atomic interactions at liquid interfaces. When little is known about these atomic interactions, γ and $(-\partial\gamma/dT)$ can be determined by experimental methods. Using Eotvos equation a value of 0.31 $mNm^{-1}K^{-1}$ was found for liquid copper as compared to -.20 using the emperical relation above. However using the following equation:

$$\partial\gamma/dT = Vmp \,/\, (Tc-Tmp) \qquad \ldots . \quad (7.5)$$

where Tc is the critical temperature, Vmp is the volume at the melting point and Tmp is temperature at melting point, a value of 0.21 was obtained.

Srinivasan, et al (21) compared several empirical relationship on temperature dependence of surface tension. Among these were the Macleod's equation:

a) $$(\gamma^{1/4}/\rho) = km \;\; W \qquad \ldots . \quad (8.5)$$

where γ is surface tension, ρ is density and km a constant. W is a calibration value used in the modified Wilhelmy plate method.

b) Sugden's parachor equation: $$(\gamma^{1/4}M)/\rho = P \qquad \ldots . \quad (9.5)$$

where M is the molecular weight and P the parachor.

c) The Eotvos, Ramsay and Shield's equation, previously discussed as Eotvos equation.

d) The Ferguson's equation: $$\gamma = \gamma o \,(1-\theta/\theta_c)^n \qquad \ldots \quad (10.5)$$
where γ is the surface tension at θ°C, γ_o the surface tension at 0°C, θ_c is the critical temperature in °C. and n is a constant.

e) The Van-der-Waals equation mentioned previously.

They found one relationship that established the equivalence of all five equations. This was a constnt K that established a relationship connecting Eotvos constant, the Ferguson constant, and the Sugden parachor P =Mkm and is defined as:

$$K=\gamma_o^{5/6}P^{2/3}/\theta_c \qquad \ldots\ldots (11.5)$$

Heat Transfer and Surface Tension

Temperature effects on surface tension find much relevance in heat transfer studies. Alamgir and Leinhard (22) correlated, the temperature dependence of the surface tension of pure liquids with the law of corresponding states, where the molecular form is characterized by the Pitzer acentric factor w.

$$w = -1 + \log_{10} P_{rs} \ (T_{rs} = 0.7) \qquad \ldots\ldots (11.5)$$

T_{rs} and P_{rs} are the reduced saturation pressure and temperature respectively. They found that when the Pitzer factor reached the Van-der-Waals value their function reduces to a form identical to the Van-der-Waals limiting liquid super heat, which is the change Δ Tm between "spinodal temperature Tm", and saturation temperature Ts.

$$\gamma \tilde{-} (1-T_{rs})^{3/2} \qquad \ldots\ldots (12.5)$$

Tm is the point at which $(\partial P/\partial V)T \to 0.$, i.e. the last temperature on the stable portion of a liquid isotherm. Van-der-Waals considered the change in chemical potential through a surface layer by:

$$\gamma_{vdW} \tilde{-} (1-T_{rs})^{3/2} \qquad \ldots\ldots (13.5)$$

Numerical techniques were used in their determinations and they found a functional dependence of surface tension on 'w' and temperature,in equation (14.5). T_{rm} is the reduced spinodal temperature.

$$\gamma(T_{rs},w) = \gamma o(w)\ [\Delta T_{rm})vdW]^{\ f_3(w)} \ldots\ldots (14.5)$$

For all substances but water and for $\Delta T_{rs} \leq$ A.84 ,they found both high and lower or moderate temperature correlations.

Polarography

Quantitative determination of material in solution using polarography depends on the amount of material adsorbed on a working mercury electrode. Any decreases in adsorption of material with temperature increases can be observed in the polarogram. Present day polarography is used extensively in the study of residual material such as surfactants in solution. The precautions established by the work of Danilov et al (23) prove useful for this application. They investigated the effects of temperature on the adsorption of tertiary butyl alcohol on mercury and they observed that with increasing temperature a decrease in the adsorption peaks. The equilibrium degree of coverage θ was found to decrease with increasing temperature (see Fig 6).

The "Critical" temperature obtained at maximum $(\frac{\partial\theta}{\partial T})_{C,E}$ depended on the nature of the adsorbate and the solution composition (E = electrode potential and C = concentration) . Their calculations showed an increase in ΔS^{o}_{θ} with increasing θ. This was attributed to decomposition of the structured layer of the solvent, and dehydration of the surfactant, which occured during adsorption. Desorption of water occured with increasing θ. The increase in ΔS^{o}_{θ} determines the value of ΔG^{o}_{θ} from the third law of thermodynamics. Since $\partial\Delta H^{o}_{\theta}/\partial\theta$ was ≤ 0 , they concluded that there was little or no interaction between adsorbed molecules. Here structural entropy played a predominant role in adsorption behaviour. The thermodynamic parameters of adsorption was influenced greatly by the adsorption of a water layer on the working mercury electrode. All the thermodynamic properties ΔG^{o}_{θ}, ΔH^{o}_{θ} and ΔS^{o}_{θ}, were dependent on the electrode potential.It must be noted that a positively charged surface caused a higher surface bonding of water than a negative surface.

Surfactants, Interfacial Tension and Temperature Dependence

Temperature dependence of surface tension has been studied in relation to surfactant type and concentrations. These studies have commanded a great deal of interest especially for enhanced oil recovery applications. The general trend as expected is that the surface tension decreases as temperature is increased. However the shapes of the interfacial tension versus temperature curves are sources of information on the mechanisms of interactions of the different types of surfactants or the

possibility of detection of chemical changes of the adsorbate or adsorbent with temperature.

Takasawa et al (24) looked at the surface tensions of polyethylene-glycol-n-ethers of varied polyethylene chain lengths with a surfactant such as SDS (sodium dodecyl sulfate) at 15°, 25° and 40°C respectively. They observed that the width of the flat portion of the surface tension versus concentration of the mixed SDS and nonionic surfactants curves, decreased with shorter chain length of polyoxyethylene. This is analogous to the commonly known Traube's rule for homologous series (1).

A rise in temperature gave the same effect as the shorter chain lengths. Since the flat portion occured in the same concentration range for which mixed micelles are present in solution, the temperature effect would give more information on mixed micelles , as well. They related the decrease in the length of the plateau to dehydration of ethylene oxide chain adsorbed in the water surface.

A plot of surface pressure versus the inverse concentration for each chain length at 15 25, 40°C respectively showed that the plot features were similar to adsorbed surface films of mixed surfactants in a two dimensional state. This was analogous to the p-V isotherm of a three dimensional gaseous state obeying the Van-der-Waals equation. The chain lengths (C_{12} E_m, m = 0 to 8) of the ethylene oxide unit at m=3, produced the plateau, which, disappeared between 15° to 40°C. This was the critical length for mixed micelles.

A similar set of experiments was again carried out using octaethylene glycol-n-alkyl-ether (25) (C_nE_8 : n = 10 to 14) in the presence of SDS (6.3 mM), at 15°C to 40°C. It was found that the length of the plateau decreased in n=8 to n=4 region for ethylene oxide unit. The values for the critical alkyl chain length for each temperature, suggested that mixed micelles could be formed only by nonionics with alkyl chain length longer than given values as shown below.

		15°C	25°C	40°C
Critical Ethylene Oxide chain length	$C_{12}Em$	m = 3.5	m = 37	m = 3.9
Critical Alkyl chain length	CnE_8	n= 1.8	n = 2.3	n = 2.6

Gillap et al earlier (26) studied the effect of temperature on the ideal adsorption of SDS and SDDS at the dodecane/0.1M NaCl interface. There was a decrease in γ with increasing temperature. This data was used to determine ΔG^{o}, as a function of temperature. ΔS^{o} was also determined. The thermodynamic data indicated that the major driving force to adsorption at hydrocarbon-water interface was entropic rather than enthalpic. The negative ΔG^{o} of adsorption of SDS, SDDS was greater at the O/W interface than the air/water interface. ΔS^{o} was also greater at O/W than W/A (Fig. 7, Table 3).

Standard thermodynamic functions for adsorption of SDS and SDDS showed a decrease in ΔG^{o} with increasing chain length of surfactant because of increased ΔH^{o} and $T\Delta S^{o}$. The $T\Delta S^{o}$ was greater at oil/water interface than water/air interface.

The loss of structured water at the interface contributed to the entropy gain. Hydrophobic bonding increased with this loss. SDDS dimers dissociated upon adsorption at the O/W interface and hence increased the entropic contribution to the adsorption process. The enthalpic effect therefore, when this occurred was positive, since dimers are more stable in the bulk. As the surfactant penetrated the oil phase, separation of oil molecules resulted in an enthalpic effect, possibly associated with forces of adhesion between the alkyl chains of the oil and the surfactant molecules. The negative enthalpy from the interaction and penetration was greater than the positive enthalpy from separation of the oil.

Results such as these indicate the relevance of thermodynamic studies for enhanced oil recovery applications.

Temperature Dependance at the Oil-Water Interface

Aveyard (13) reported that surface pressures at surface saturation for most surfactants at the air/water surface is around 20 to 40 mNm^{-1}. The lowest γ is around 30 mNm^{-1}. He suggested that at the oil/water interface γ_i could be lower. Obtaining ultralow γ_i is of crucial importance in microemulsion formation and for enhanced oil recovery studies. Using well defined conditions, such low anionic surfactants concentration in dilute NaCl, and fixed temperature, ultra low alkane/water tensions can be found.

When γ_i was studied as a function of temperature with a nonionic surfactant and using a spinning drop technique, in a region of minimum

tension, a fluid phase ∂ was formed (Fig. 9). The density in this phase was intermediate between the densities of the two major α and β phases. With high temperatures, the surfactant would reside in the oil phase, and at low temperatures the surfactant was in the water phase. Observations of the oil droplet in the water within the spinning drop apparatus were as follows: as temperature decreased the drop was coated with the ∂ phase. At low γ_i, the drop formed discrete segments of ∂ and α (Fig. 9). The minimum temperature was the phase inversion temperature (PIT).

Sontag and Strenge (27), reported that coalescence stability was not necessarily due to surfactant desorption that occur only with thermal energy. They attributed coalescence as due to changes in mechanical properties of the adsorption layer with increasing temperature (Fig.10). Black films formed at 20°C with the emulsifier span 80, was not affected when heated to 75°C. With span 80 at varied concentrations, octane/.05m KCl emulsions showed specific temperatures of coalescence. These were not necessarily at minimum γ.

Crude Bitumen

There are limited publications in relation to surface tension of bitumen studied as a function of temperature for field applications,. The surface entropy term $-\partial\gamma/\partial T$ was found by Potoczny et al (28) to be lower for bitumen extracted with organic solvents, than the bitumen extracted by centrifugation. The general observation was that surface entropy decreased with the increasing molecular size of the soluble molecular units. They claimed that the solvent extracted bitumen had larger molecules than the centrifuged bitumen. The larger molecules had higher γ. The toluene decreased the γ of bitumen, and the temperature of extraction did not change the γ. Also mechanical extraction over a long period of time decreased the surface tension but increased the surface entropy. This is an area of study much needed in the applications of thermodynamics.

Temperature Dependence in Biochemical Systems

In biological systems changes in surface tension with temperature are most often associated with conformational changes of the protein molecule. Decreased surface entropy often results in these rearrangements. Using a modified Wilhelmy plate technique in the temperature scanning mode,

Purdon, Tinker and Neumann (29) studied surface conformational properties of the Egg lysolecithin-water solutions. They found the temperature dependence of the critical micelle concentration (CMC) of the lipid from 20°C to 80°C. From the CMC values, they calculated ΔH of micellization using least squares analysis. Because of conformational changes of the monomer none of the γ versus T(temperature) plots were linear.

$$\Delta H_{mic} = 2.303\ R\ \frac{d\ \log\ (CMC)}{d\ (1/T)}$$

There was also a temperature dependent increase in solubility of the micellar phase, in the CMC region. Desorption from the surface occured, resulting in increase in surface tension. Changes in structures of proteins or polymers can be indicated by such surface tension data.

Temperature Dependence and Polymers

Adsorption of polymers is influenced by many factors, including solvents, surfaces of adsorbents, molecular weight and concentration of polymers. However polymer solutions in the theta temperature region are closer to ideality than at other temperatures. In this region the polymers experience critical miscibility. The excess Gibbs free energy of mixing increases near this region, and decreases at temperatures above it. In this region Okubo and Ueberreiter (30) investigated the work of two researchers, Ferroni and Mersenheimer whose results were contradictory. Feroni found that $d\gamma/dT$ changes sign abruptly in the theta temperature range whereas Mersenheimer's did not, and suggested that the time dependence of heating was the cause.

The work of Okubo and Ueberreiter was done in order to solve a difference of opinion between the two researchers. Using a modified Wilhelmy method for temperature gradients,Okubo and Ueberreiter found no transition at the theta temperature and suggested that a non equilibrium curve was the cause of the transition observed by Ferroni et al. They concluded that continuous surface tension measurements can be regarded as equivalent to equilibrium measurements since they found identical results for either methods.

This is only one area in which temperature dependence studies prove useful for polymers. In polymer interactions at an interface, temperature

influence the conformation of the polymer for adsorption and hence the surface entropy which in many cases governs adsorption. Polymer flooding in bitumen recovery processes experience high temperatures in the earth's interior. Although the mechanism of polymer adsorption is quite complex and are dependent on many operational factors, some work in this area could be quite useful.

CONCLUSION

Interfacial thermodynamics treated in this study, described an intricate relationship between the interfacial tension and adsorption. In this treatment, the structure and energetics of pure liquid/vapour, liquid/liquid, and solid/liquid interfaces were first described. The thermodynamics of the interfaces were treated in detail.

The Gibb's mathematical plane which is the simplest expression of describing surface excess properties does not account for molecular dimensions. It also does not make any assumptions about the nature of the adsorbing process. It deals with relatively simple systems, as it was originally derived for liquid/liquid planar interfaces. However it is used frequently because of the convenience and simplicity.

The Guggenheim-Adams model is important when the volume of the interface matters. This model is appropriate for polymer adsorption in some cases. The mathematics become more complex since adsorption takes on a finite thickness at the interface. Guggenheim-Adams model was a means of expressing the adsorption equation relating surface tension to the concentration of adsorbing species, in terms of mass, volume and moles relative to the bulk.

The necessary precautions and assumptions made in the study of interfaces were discussed in relation to use of particular models. When the system under study became complex in terms of the solids, or liquid mixtures simplifying assumptions normally used, were shown to have particular drawbacks. The interfaces were shown to be related theoretically, depending on how one wants to define the dividing region of the Gibb's mathematical plane

Although there are many ways by which adsorption can be measured this paper has placed emphasis on those by which surface tension data can be obtained directly or derived from calorimetric data. Experimental procedures and techniques were not treated, however the use of the data was emphasized.

Temperature dependence studies are necessary for further thermodynamic characterization of many systems. This aspect was illustrated theoretically, and practically with examples taken from a broad spectrum of fields such as metallurgy, polarography, heat transfer, biochemistry, polymers, emulsion and surfactant studies. Results showed that these studies are useful for determining changes in conformation of polymers and proteins. Desorption behaviour of surfactants at an oil/water interface and ultralow tensions are temperature influenced. This is useful in microemulsion formation. The effects on coalescence of emulsions as influenced by temperature was not necessarily at the the minimum interfacial tensions of the droplets. Temperature and solvents influence the surface tensions of crude oils. Full understanding of natural surface processes requires a sound knowledge of the basics in interfacial energetics.

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Table 1(ref 9)

Methods of Measuring the Surface Tension of Single Liquids and Solutions

Method	Suitability	
	Pure Liquids	Solutions
Capillary height	Very satisfactory when the capillary wets reproducibly.	Difficult when the contact angle is not 0°C or variable
Sessile drop	Very satisfactory.	Very useful for studying surface ageing.
Pendent drop	Very satisfactory but has experimental difficulties.	Useful for studying surface ageing
Wilhelmy plate	With a good experimental set up, very accurate and convenient.	Provides accurate data on surface ageing.
Maximum pull on a cylinder	Very satisfactory. Easy to operate with simple apparatus.	Satisfactory if used with care and small displacements near maximum pull.
Maximum pull on a cone	Similar to cylinder method, but since the cone constant is universal, the results are easier to calculate.	
Du Nouy ring	Satisfactory	Unsatisfactory
Drop weight or drop volume	Very satisfactory	Poor when ageing effects suspected.
Maximum bubble pressure	Has experimental problems but useful where other methods are difficult to use.	Gives problems with ageing solutions.

Table 2 (ref 9)

The Surface and Interfacial Tensions of Some Liquids (γ/mN m^{-1}) at 293.2K Together with Values of W_A^{123}/mJ m^{-2} and ($d\gamma/dT$)mN $m^{-1}K^{-1}$

	γ	W_A^{123}		$-d\gamma/dT$	
	Liquid/vapour	Water/Liquid	Water/liquid	Liquid/vapour	Water/Liquid
Water	72.75			0.16	
Octane	21.69	51.68	42.76	0.095	0.09
Dodecane	25.44	52.90	45.29	0.088	0.09
Hexadecane	27.46	53.77	46.44	0.085	
Benzene	28.88	35.0	66.6		
Tetrachloromethane	26.77	45.0	54.5		
Octanal	27.53	8.5	91.8		
Butanol	24.6	1.6	95.8	0.082	
Aminobenzene	42.9	5.9	109.8		
Diethylether	17.0	10.7	79.1		
Ethylethanoate	23.9	~3	~94		
Mercury	484	426	131		

TABLE 3 (ref.26)

Comparison of Standard Thermodynamic Functions for Adsorption at the Air-Water and Dodecane-Water Interfaces for Sodium Decyl Sulfate and Sodium Dodecyl Sulfate at 25°

ΔG° (air-water), kcal/mol	-5.92	-7.31
ΔG° (oil-water), kcal/mol	-8.00	-8.83
Δ(ΔG°), kcal/mol	-2.08	-1.52
ΔH° (air-water), kcal/mol	-2.0	-3.3
ΔH° (oil-water), kcal/mol	-2.0	-1.2
Δ(ΔH°), kcal/mol	-0.9	2.1
ΔS° (air-water), eu	13	13
ΔS° (oil-water), eu	17	25
Δ(ΔS°), eu	4	12

Table 4

Common Methods of Measuring Contact Angle

Solid Surface	Technique	Comments
Flat	Direct measurement from drop profile	Either sessile drop or bubble, with measurement either via a telescope with goniometer eyepiece or photographs. Can be accurate to $\pm 1°$ in the range $30 < \theta < 150°$.
Flat	Calculations from drop profile using the Young-Laplace equation	A two-parameter fit is usual (e.g. drop height and maximum diameter is usually used for $\theta > 30$). For $\theta < 30°$, drop height and diameter of contact circle can give very accurate results ($\pm 0.1°$). Note: Use Hartland and Hartley (1976) rather than the Bashforth-Adams tables recommended by Neumann and Good. γ can be determined simultaneously.
Flat	Wilhelmy plate	Measurement of θ is reduced to the measurement of a weight, which can be very accurate. The method is restricted to materials that can be prepared as flat plates of constant perimeter and constant surface morphology on all faces.
Flat	Capillary rise at a vertical plate	Capable of $\pm 0.1°$ reproducibility i.e. an order of magnitude better than direct measurement.
Flat	Tilting plate	The apparatus is simple, but it is not easy to be sure whether a retreting or advancing angle, or something in between, is being measured.
Flat(with smooth reflecting surface)	Interference microscopy	Useful for sessile drops on polished crystal faces or lenses of one liquid on another. Very accurate for $\theta < 15$. (Fringes become too

		close at higher θ.) Requena et al. (1975); Callaghan et al.(1983).
Transparent tube	Capillary rise	Restricted to small diameter tubes. Not recommended for liquid mixtures with low concentrations of an adsorbable component.
Transparent tube	Reflection from liquid surface	Particularly good for highly reflecting surfaces, e.g. liquid metals.
Cylinders, rods, fibres	Direct measurement	Rather difficult experimentally. The curvature of the solid surface can induce large experimental errors, which can be minimized by keeping the drops sufficiently small.
	Floating fibre	Good fun, but experimental accuracy is severely limited by optical resolution required to measure small vertical displacements.
	Wilhelmy method	Probably the best, provided that the perimeter of the fibre can be accurately measured (this can be a severe limitation).
Bundles and mats of fibres		There is no good method for measuring contact angles. Do not mixtake the angle of a drop on a mat for the angle of contact with the individual fibres!
Powders (spherical particles)	Floating particle	
Powders (irregular particles)	Time taken to sink	Qualitative only.
Powders (compressed cake)	Direct measurement of macroscopic angle	At best. useless. At worst positively misleading.

Liquid penetration	Several methods are available (volume, pressure, rate of penetration etc.), all of which give results which at least have some meaning, although that meaning is usually model-dependent.

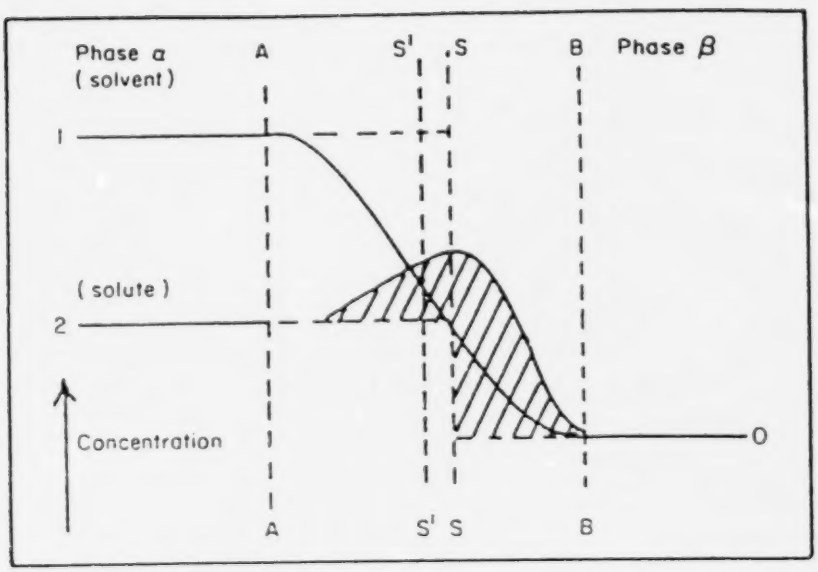


Fig. 1 - Model of adsorption in the surface phase showing thickness at the interphase S-S'. (After ref. 14)

(a) Hypothetical interface . Sharp boundary

(b) Real interface, total amount of 2 unchanged. No adsorption

(c) Boundary with adsorption. There is more 2 in the region shown, but less of 1. This is the +ve adsorption of solute and -ve adsorption of solvent

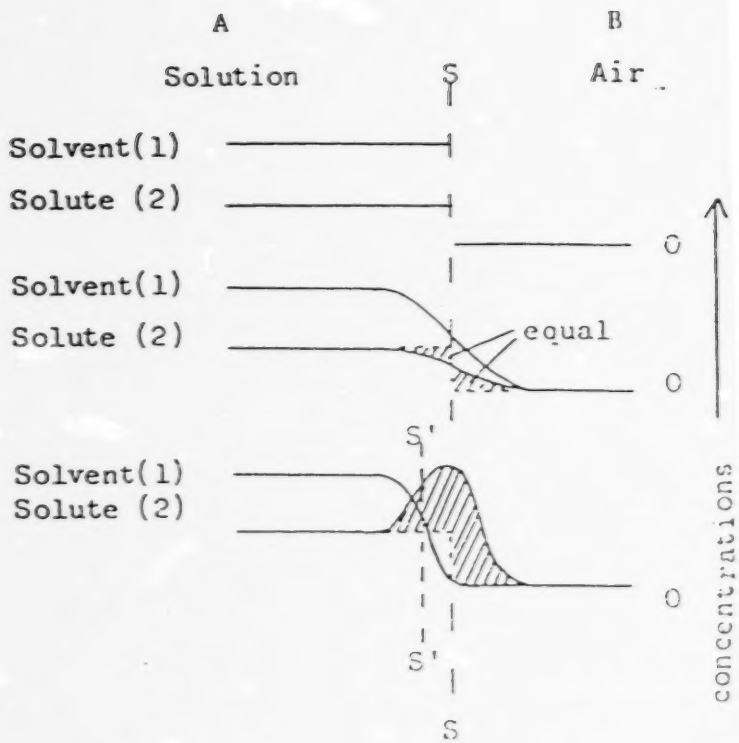


Fig. 2a. - Schematic explaining the changes in structure at the interface when adsorption occurs. S-S' is the Gibb's dividing plane. (Adapted from ref. 8).

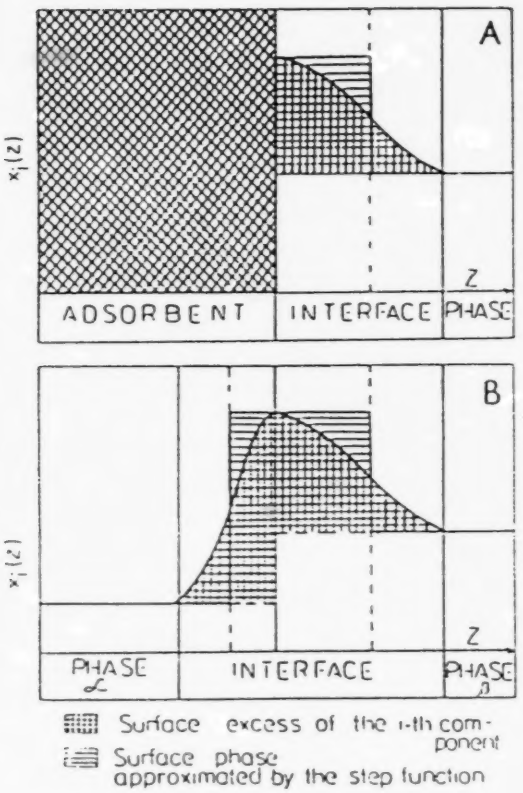


Fig. 2b. - Concentration profiles for adsorption processes occuring at solid/liquid (A) and liquid/liquid (B) interfaces. (After ref. 2).

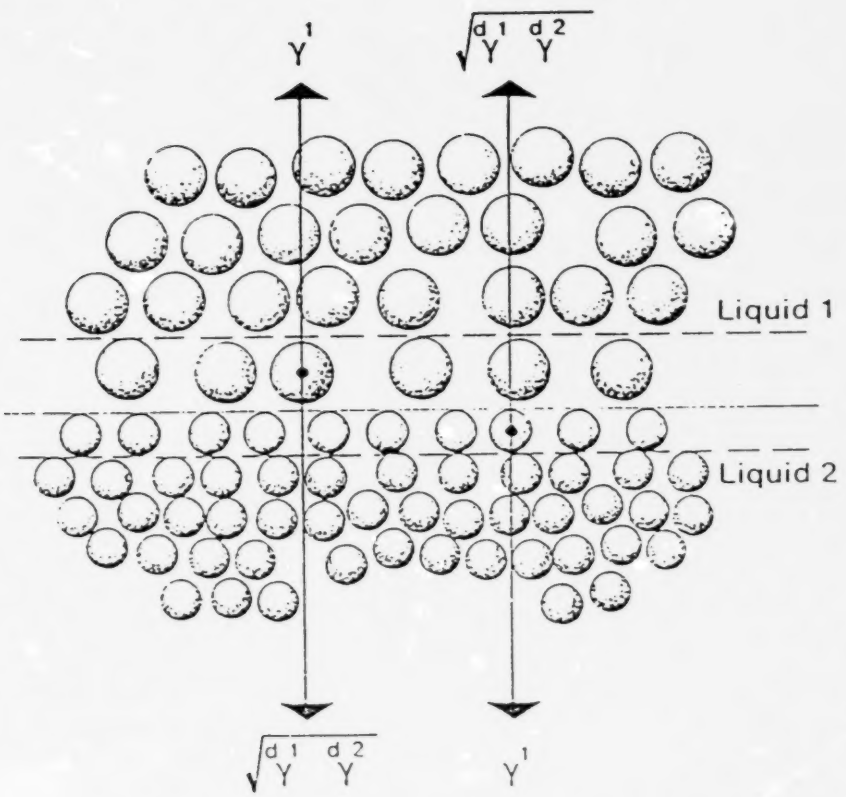
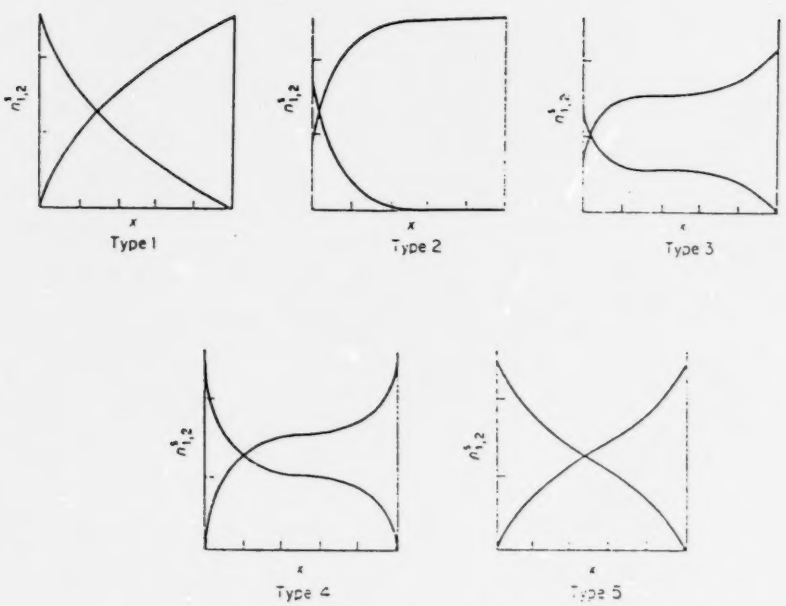


Fig. 3 - The Fowkes model of the liquid-liquid interface. (Ref. 9).



Type 1 - No preferential adsorption eg. adsorption from mixtures of ethylene chlonde on silica gel.

Type 2 - Inflection U-shaped. Strongly curved almost conforming to Langmuir (from mixtures of benzene and ethyl alcohol on charcoal).

Type 3 - Occurs when molecular sieve action occurs (s-shaped).

Type 4,5 Variations of type when departure from linearity is observed (e.g. ethylene dichloride and benzene on charcoal).

Fig. 4. - Types of individual isotherm according to Schay.[31] (Reproduced with permission from Periodica Polytechnica.)

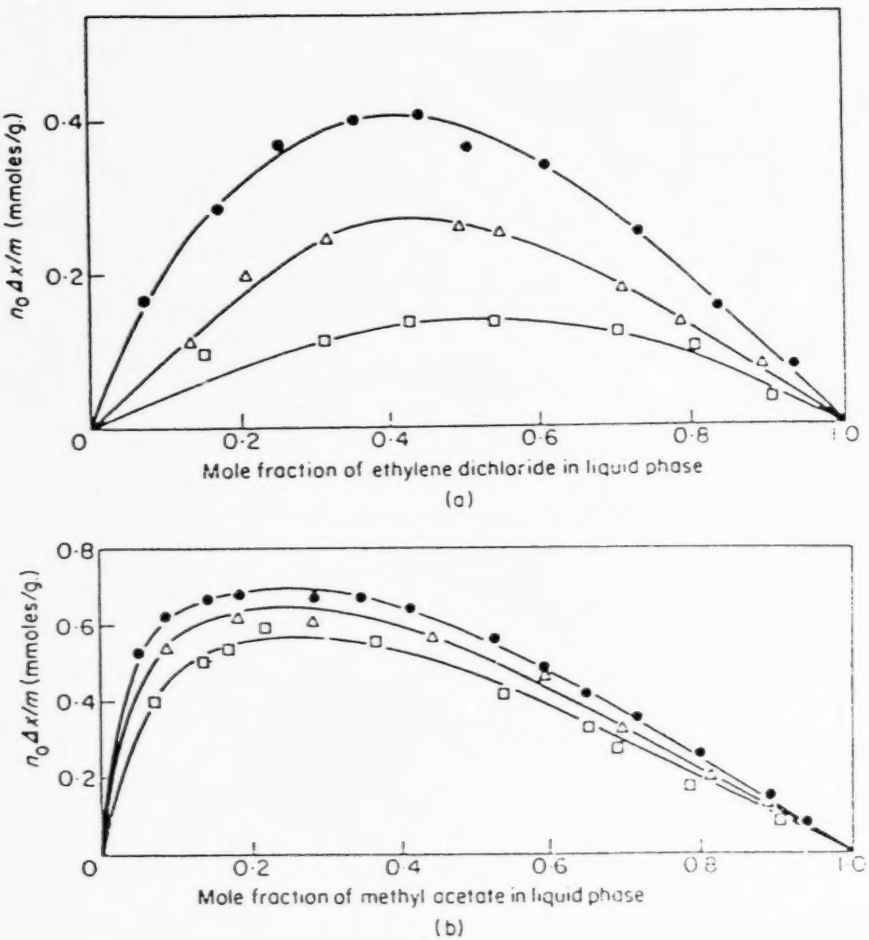


Fig. 5 - Effect of temperature on adsorption by alumina (boehmite) from mixtures of (a) ethylene dichloride and benzene, (b) methyl accetate and benzene: O, 20°C; Δ, 40°C. (Adapted from ref. 1).

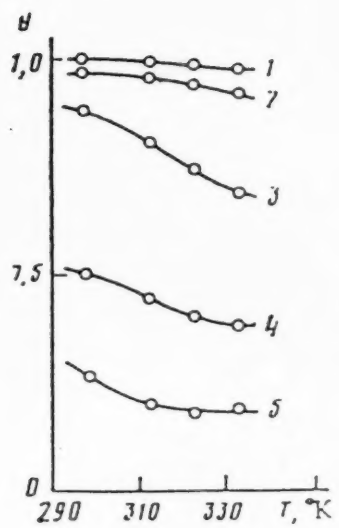


Fig. 6. - Change in the degree of coverage of the Mercury electrode with the temperature at various TBA concentrations, M: 1) 0.4; 2) 0.2; 3) 0.1: 4) 0.06; 5) 0.05. Electrolyte: 1 N H_2SO_4. (After ref. 23).

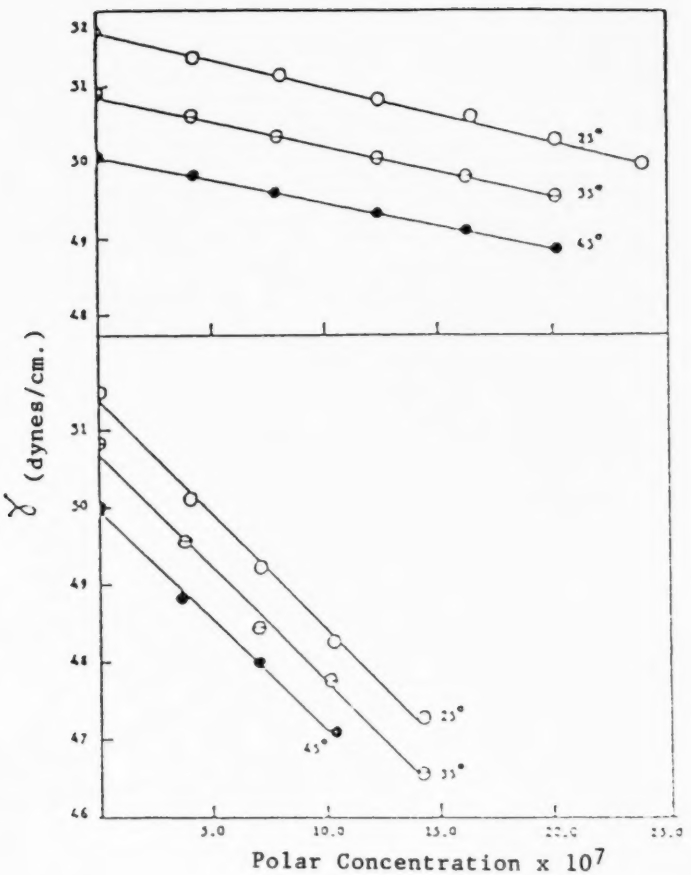


Fig. 7 - Interfacial tension (γ) vs. molar concentration of sodium decyl sulfate (upper plot) in the ideal region (dodecane system) at 25 (O), 35 (Θ), and 45° (●). (After Gillap 26).

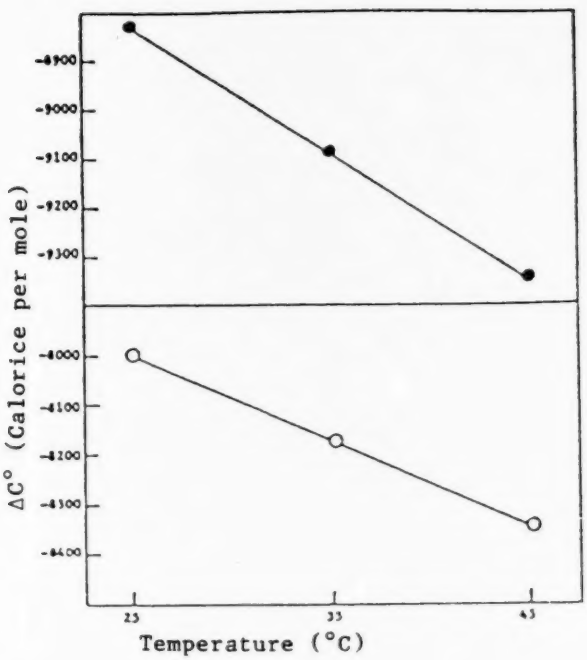


Fig. 8. - Standard free energy of adsorption (ΔG°) plotted as a function of temperature from interfacial tension data for sodium decyl sulfate (O) and sodium dodecyl sulfate (●) at the dodecane-0.1 M NaCl interface.(After ref. 26).

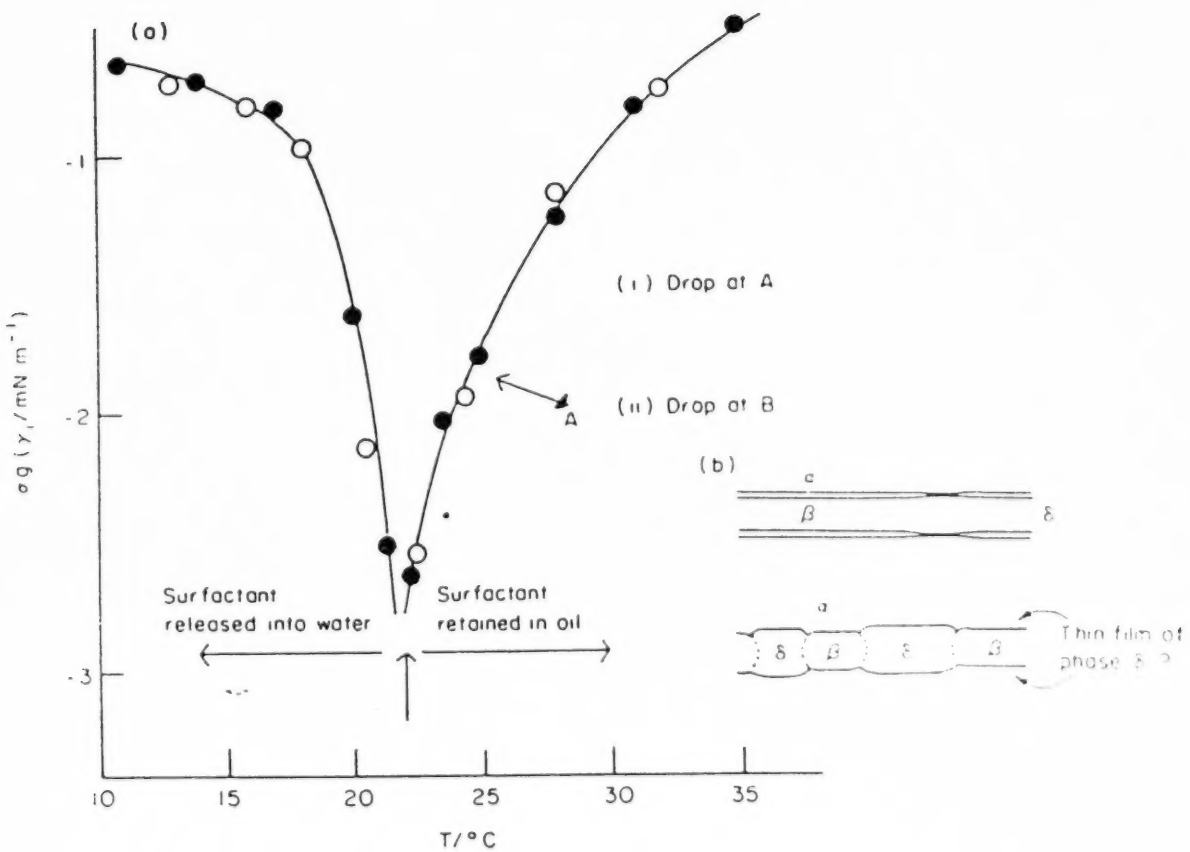


Fig. 9. - Effect of temperature on γ_i between 5 x 10^{-4}M $C_{12}E_4$ in 5 g ℓ^{-1} aqueous NaCl and 5% W/W $C_{12}E_4$ in dodecane. (a) ● for new oil samples at each T, O for 35°C sample cooled down. (b) Appearance of oil drop in spinning-drop apparatus at two temperatures. (After ref. 13).

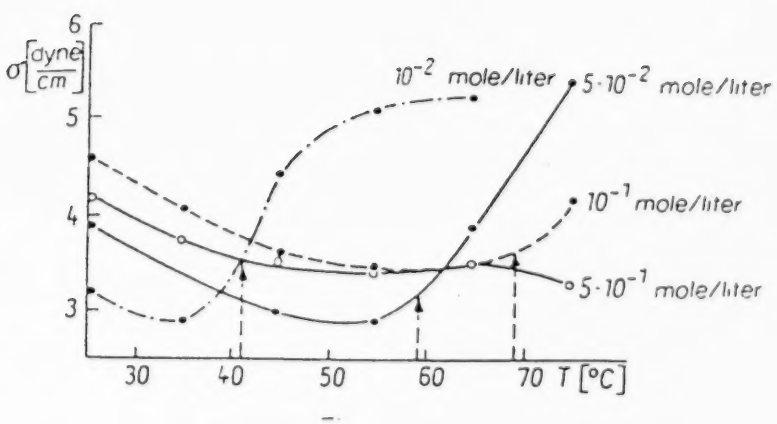


Fig. 10. - Surface tension vs. temperature for various solutions of Span 80 in octane against 0.05M KCl[5]. Arrows indicate temperatures at which coalescence sets in. (After ref. 27).